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(54) Title: MAGNESIUM DICHLORIDE-ALCOHOL ADDUCTS AND CATALYST COMPONENTS OBTAINED THEREFROM

(57) Abstract: The present invention relates to  $MgCl_2 \cdot (EtOH)_m \cdot (ROH)_n \cdot (H_2O)_p$  adduct in which R is a C1-C15 hydrocarbon group different from ethyl, n and m are indexes, higher than 0, satisfying the equations  $(n+m) \geq 7$  and  $0.05 \leq n/(n+m) \leq 0.95$  and p is a number ranging from 0 to 0.7 with the proviso that when R is methyl and (n+m) is in the range of 0.7 to 1, the value of n/(n+m) ranges from 0.05 to 0.45. The catalyst components obtained from the adducts of the present invention are capable to give catalysts for the polymerization of olefins characterized by enhanced activity with respect to the catalysts prepared from the adducts of the prior art.

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**TITLE:****“Magnesium dichloride-alcohol adducts and catalyst components obtained therefrom”**

The present invention relates to adducts between magnesium dichloride, ethanol and specific amounts of other alcohols. The adducts of the present invention are particularly useful as precursors of catalyst components for the polymerization of olefins.

MgCl<sub>2</sub>•alcohol adducts and their use in the preparation of catalyst components for the polymerization of olefins are well known in the art. Catalyst components for the polymerization of olefins, obtained by reacting MgCl<sub>2</sub>•nEtOH adducts with halogenated transition metal compounds, are described in USP 4,399,054. The adducts are prepared by emulsifying the molten adduct in an immiscible dispersing medium and quenching the emulsion in a cooling fluid to collect the adduct in the form of spherical particles. No physical characterization regarding the degree of crystallinity of the adducts is reported.

In WO98/44009 are disclosed MgCl<sub>2</sub>•alcohol adducts having improved characteristics and characterized by a particular X-ray diffraction spectrum, in which, in the range of 2θ diffraction angles between 5° and 15°, the three main diffraction lines are present at diffraction angles 2θ of  $8.8 \pm 0.2^\circ$ ,  $9.4 \pm 0.2^\circ$  and  $9.8 \pm 0.2^\circ$ , the most intense diffraction lines being the one at  $2\theta = 8.8 \pm 0.2^\circ$ , the intensity of the other two diffraction lines being at least 0.2 times the intensity of the most intense diffraction line. Said adducts can be of formula MgCl<sub>2</sub>•mEtOH•nH<sub>2</sub>O

where m is between 2.2 and 3.8 and n is between 0.01 and 0.6. In addition to the above described X-ray spectrum, the adducts are characterized by a Differential Scanning Calorimetry (DSC) profile in which no peaks are present at temperatures below 90°C or, even if peaks are present below said temperature, the fusion enthalpy associated with said peaks is less than 30% of the total fusion enthalpy. The catalyst components obtained from these adducts have an increased activity over those obtained from the adducts of the prior art. However, the availability of catalyst components with still improved activity is always needed in view of the economic advantages obtainable in the operation of the industrial plants.

EP 123767 discloses a catalyst component obtained by reacting a titanium compound and a vanadium compound with a solid support obtained by the spray drying of MgCl<sub>2</sub> in a mixed solution of methanol and ethanol. The spray-dried support contains a low amount of total alcohol content (about 1 mole or less of total alcohol per mole of MgCl<sub>2</sub>) in combination with a generally high molar content of methanol with respect to ethanol. The activity shown by

these catalysts are generally low and in particular it does not improve by partial replacement of the ethanol with methanol. In fact, example 2 in which only ethanol is used has the highest productivity.

The applicant has now found that it is possible to improve the polymerization activities of the catalyst of the prior art when the catalyst component is prepared by starting with supports containing  $MgCl_2$ , ethanol and another alcohol in specific proportions.

The present invention therefore relates to  $MgCl_2 \cdot (EtOH)_m(ROH)_n(H_2O)_p$  adducts in which R is a C1-C15 hydrocarbon group different from ethyl, optionally substituted with heteroatoms containing groups, n and m are indexes, higher than 0, satisfying the equations  $n+m \geq 0.7$  and  $0.05 \leq n/(n+m) \leq 0.95$  and p is a number ranging from 0 to 0.7 with the proviso that when R is methyl and (n+m) is in the range of 0.7 to 1, the value of n/(n+m) ranges from 0.05 to 0.45.

Preferably, (n+m) is higher than 1 and in particular it ranges from 2 to 5. In a particular aspect, the value n/(n+m) ranges from 0.1 to 0.4 and preferably from 0.15 to 0.35. The index p typically ranges from 0.01 to 0.6 and particularly from 0.01 to 0.4. Preferred R groups are methyl and C3-C10 saturated hydrocarbon groups, in particular methyl and C3-C8 alkyl groups. Specific examples of ROH alcohols according to the invention are methanol, propanol, isopropanol, n-butanol, i-propanol, sec-butanol, tert-butanol, pentanol, 2-methyl-1-pentanol, 2-ethyl-1-hexanol, phenol, 4-methyl-1-phenol, 2,6-dimethyl-1-phenol, cyclohexanol, cyclopentanol. Methanol, n-butanol, sec-butanol, i-propanol, and 2-methyl-1-pentanol are preferred. Methanol is especially preferred.

The adducts of the present invention can be prepared according to several methods. According to one of these methods the adducts are prepared by contacting the desired amounts of  $MgCl_2$  ethanol and ROH alcohol, optionally in the presence of an inert liquid diluent, heating the system at the melting temperature of  $MgCl_2EtOH$ -alcohol adduct or above, and maintaining said conditions so as to obtain a completely molten adduct. Said molten adduct is then emulsified in a liquid medium which is immiscible with and chemically inert to it and finally quenched by contacting the adduct with an inert cooling liquid thereby obtaining the solidification of the adduct. In a specific embodiment of this method the adduct is kept at a temperature equal to or higher than its melting temperature, under stirring conditions, for a time period equal to or greater than 10 hours, preferably from 10 to 150 hours, more preferably from 20 to 100 hours. The liquid in which the molten adduct is emulsified can be any liquid immiscible with and chemically inert to the molten adduct. For example, aliphatic,

aromatic or cycloaliphatic hydrocarbons can be used as well as silicone oils. Aliphatic hydrocarbons such as vaseline oil are particularly preferred.

An alternative way for obtaining the adduct of the invention in solid form comprises the formation of the molten adduct as disclosed above and the use of an associated spray-cooling process for solidifying the adduct. When this option is pursued it is preferred that in the first step the magnesium chloride, the ethanol and the ROH alcohol be contacted to each other in the absence of an inert liquid diluent. After having been molten the adduct is sprayed, through the use of the proper devices that are commercially available, in an environment having temperature so low as to cause rapid solidification of the particles. The cold environment can comprise a cold liquid or gas. In a preferred aspect the adduct is sprayed in a cold liquid environment and more preferably in a cold liquid hydrocarbon.

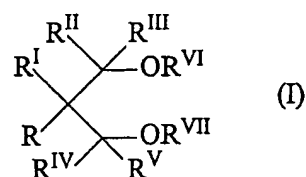
Another usable method comprises contacting a ROH alcohol with an already preformed solid  $\text{MgCl}_2$ -ethanol adduct. The contact between the desired amounts of  $\text{MgCl}_2$ -ethanol adduct and the ROH alcohol can be carried out in liquid hydrocarbon medium under stirring conditions. It is also possible to add the ROH alcohol in a vapor phase, and particularly in a loop reactor as described in WO98/44009. It would be particularly preferred to use a  $\text{MgCl}_2$ -ethanol adduct in which part of the ethanol has been removed by physical (for example under a hot nitrogen stream) or chemical dealcoholation. These dealcoholated adducts and their preparation are described for example in EP395083 the relevant part of which is included by reference.

All these methods provide solid adducts having a substantially spherical morphology which are particularly suitable in the preparation of spherical catalyst components for the polymerization of olefins and in particular for the gas-phase polymerization process. With the term substantially spherical morphology are meant those particles having a ratio between the greater and smaller axis equal to or lower than 1.5 and preferably lower than 1.3.

As explained above while water may be one of the constituents of the adduct too high levels of it should preferably be avoided. In doing that, it can be useful to control the water content of the reactants. In fact,  $\text{MgCl}_2$ , EtOH and also certain ROH alcohol are highly hygroscopic and tend to incorporate water in their structure. As a result, if the water content of the reactants is relatively high, the final adducts may contain an undesired amount of water even if it has not been added as a separate component. Means for controlling or lowering the water content in solids or fluids are well known in the art. The water content in  $\text{MgCl}_2$  can be for example lowered by drying it in an oven at high temperatures or by reacting it with a compound which

is reactive towards water. As an example, a stream of HCl can be used to remove water from  $\text{MgCl}_2$ . Water from the fluids can be removed by various techniques such as distillation or by allowing the fluids to become in contact with substances capable to subtract water such as molecular sieves.

As mentioned above these adducts can be advantageously used in the preparation of catalyst components for the polymerization of olefins. The said catalyst components can be obtained by contacting the adducts of the invention with compounds of transition metals belonging to one of the compound of one of the groups 4 to 6 of the Periodic Table of Elements (new notation). Among transition metal compounds particularly preferred are titanium compounds of formula  $\text{Ti}(\text{OR})_n\text{X}_{y-n}$  in which  $n$  is comprised between 0 and  $y$ ;  $y$  is the valence of titanium;  $X$  is halogen and  $R$  is an alkyl radical having 1-10 carbon atoms or a COR group. Among them, particularly preferred are titanium compounds having at least one Ti-halogen bond such as titanium tetrahalides or halogenalcoholates. Preferred specific titanium compounds are  $\text{TiCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{Ti}(\text{OBu})_4$ ,  $\text{Ti}(\text{OBu})\text{Cl}_3$ ,  $\text{Ti}(\text{OBu})_2\text{Cl}_2$ ,  $\text{Ti}(\text{OBu})_3\text{Cl}$ . Preferably the contact is carried out by suspending the adduct in cold  $\text{TiCl}_4$  (generally  $0^\circ\text{C}$ ); then the so obtained mixture is heated up to  $80$ - $130^\circ\text{C}$  and kept at this temperature for 0.5-2 hours. After that the excess of  $\text{TiCl}_4$  is removed and the solid component is recovered. The treatment with  $\text{TiCl}_4$  can be carried out one or more times. The reaction between transition metal compound and the adduct can also be carried out in the presence of an electron donor compound (internal donor) in particular when the preparation of a stereospecific catalyst for the polymerization of olefins is to be prepared. Said electron donor compound can be selected from esters, ethers, amines, silanes and ketones. As a result of this contact the electron donor compound normally remains deposited on the catalyst component. In particular, the alkyl and aryl esters of mono or polycarboxylic acids such as for example esters of benzoic, phthalic, malonic, glutaric and succinic acid are preferred. Specific examples of such esters are *n*-butylphthalate, di-isobutylphthalate, di-*n*-octylphthalate, diethyl 2,2-diisopropylsuccinate, diethyl 2,2-dicyclohexyl-succinate, ethyl-benzoate and *p*-ethoxy ethyl-benzoate. Moreover, can be advantageously used also the 1,3 diethers of the formula:



wherein R, R<sup>I</sup>, R<sup>II</sup>, R<sup>III</sup>, R<sup>IV</sup> and R<sup>V</sup> equal or different to each other, are hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and R<sup>VI</sup> and R<sup>VII</sup>, equal or different from each other, have the same meaning of R-R<sup>V</sup> except that they cannot be hydrogen; one or more of the R-R<sup>VII</sup> groups can be linked to form a cycle. The 1,3-diethers in which R<sup>VI</sup> and R<sup>VII</sup> are selected from C<sub>1</sub>-C<sub>4</sub> alkyl radicals are particularly preferred.

The electron donor compound is generally present in molar ratios with respect to the magnesium comprised between 1:4 and 1:20.

Preferably, the particles of the solid catalyst components have substantially spherical morphology and an average diameter comprised between 5 and 150 μm. With the term substantial spherical morphology are meant those particles having a ratio between the greater and smaller axis equal to or lower than 1.5 and preferably lower than 1.3.

Before the reaction with the transition metal compound, the adducts of the present invention can also be subjected to a dealcoholation treatment aimed at lowering the alcohol content and increasing the porosity of the adduct itself. The dealcoholation can be carried out according to known methodologies such as those described in EP-A-395083. Depending on the extent of the dealcoholation treatment, partially dealcoholated adducts can be obtained having an alcohol content generally ranging from 0.1 to 2.6 moles of alcohol per mole of MgCl<sub>2</sub>. After the dealcoholation treatment the adducts are reacted with the transition metal compound, according to the techniques described above, in order to obtain the solid catalyst components.

The solid catalyst components according to the present invention show a surface area (by B.E.T. method) generally between 10 and 500 m<sup>2</sup>/g and preferably between 20 and 350 m<sup>2</sup>/g, and a total porosity (by B.E.T. method) higher than 0.15 cm<sup>3</sup>/g preferably between 0.2 and 0.6 cm<sup>3</sup>/g. Surprisingly, the catalyst components comprising the reaction product of a transition metal compound with a MgCl<sub>2</sub>-alcohol adduct which is in turn obtained by partially dealcoholating the adducts of the invention, show improved properties, particularly in terms of activity, with respect to the catalyst components prepared from the dealcoholated adducts of the prior art. The catalyst components of the invention form catalysts for the polymerization of alpha-olefins CH<sub>2</sub>=CHR, wherein R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms, by reaction or contact with Al-alkyl compounds. The alkyl-Al compound is preferably chosen among the trialkyl aluminum compounds such as for example triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-

octylaluminum. It is also possible to use alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides such as  $\text{AlEt}_2\text{Cl}$  and  $\text{Al}_2\text{Et}_3\text{Cl}_3$  optionally in mixture with said trialkyl aluminum compounds..

The Al/Ti ratio is higher than 1 and is generally comprised between 20 and 800.

In the case of the stereoregular polymerization of  $\alpha$ -olefins such as for example propylene and 1-butene, an electron donor compound (external donor) which can be the same or different from the compound used as internal donor can be used in the preparation of the catalysts disclosed above. In case the internal donor is an ester of a polycarboxylic acid, in particular a phthalate, the external donor is preferably selected from the silane compounds containing at least a Si-OR link, having the formula  $\text{R}_a^1\text{R}_b^2\text{Si}(\text{OR}^3)_c$ , where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4;  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$ , are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms. Particularly preferred are the silicon compounds in which a is 1, b is 1, c is 2, at least one of  $\text{R}^1$  and  $\text{R}^2$  is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms and  $\text{R}^3$  is a  $\text{C}_1$ - $\text{C}_{10}$  alkyl group, in particular methyl. Examples of such preferred silicon compounds are methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyltrimethoxysilane, dicyclopentyldimethoxysilane. Moreover, are also preferred the silicon compounds in which a is 0, c is 3,  $\text{R}^2$  is a branched alkyl or cycloalkyl group and  $\text{R}^3$  is methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, t-butyltrimethoxysilane and hexyltrimethoxysilane.

Also the 1,3 diethers having the previously described formula can be used as external donor. However, in the case 1,3-diethers are used as internal donors, the use of an external donor can be avoided, as the stereospecificity of the catalyst is already sufficiently high.

As previously indicated the components of the invention and catalysts obtained therefrom find applications in the processes for the (co)polymerization of olefins of formula  $\text{CH}_2=\text{CHR}$  in which R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms.

The catalysts of the invention can be used in any of the olefin polymerization processes known in the art. They can be used for example in slurry polymerization using as diluent an inert hydrocarbon solvent or bulk polymerization using the liquid monomer (for example propylene) as a reaction medium. Moreover, they can also be used in the polymerization process carried out in gas-phase operating in one or more fluidized or mechanically agitated bed reactors.

The polymerization is generally carried out at temperature of from 20 to 120°C, preferably of

from 40 to 80°C. When the polymerization is carried out in gas-phase the operating pressure is generally between 0.1 and 10 MPa, preferably between 1 and 5 MPa. In the bulk polymerization the operating pressure is generally between 1 and 6 MPa preferably between 1.5 and 4 MPa.

The catalysts of the invention are very useful for preparing a broad range of polyolefin products. Specific examples of the olefinic polymers which can be prepared are: high density ethylene polymers (HDPE, having a density higher than 0.940 g/cc), comprising ethylene homopolymers and copolymers of ethylene with alpha-olefins having 3-12 carbon atoms; linear low density polyethylenes (LLDPE, having a density lower than 0.940 g/cc) and very low density and ultra low density (VLDPE and ULDPE, having a density lower than 0.920 g/cc, to 0.880 g/cc) consisting of copolymers of ethylene with one or more alpha-olefins having from 3 to 12 carbon atoms, having a mole content of units derived from the ethylene higher than 80%; isotactic polypropylenes and crystalline copolymers of propylene and ethylene and/or other alpha-olefins having a content of units derived from propylene higher than 85% by weight; copolymers of propylene and 1-butene having a content of units derived from 1-butene comprised between 1 and 40% by weight; heterophasic copolymers comprising a crystalline polypropylene matrix and an amorphous phase comprising copolymers of propylene with ethylene and or other alpha-olefins.

The following examples are given to illustrate and not to limit the invention itself.

## **CHARACTERIZATION**

### **Determination of alcohol content**

The ethanol and ROH content are determined via GC analysis.

### **Determination of X.I.**

2.5 g of polymer were dissolved in 250 ml of o-xylene under stirring at 135°C for 30 minutes, then the solution was cooled to 25°C and after 30 minutes the insoluble polymer was filtered. The resulting solution was evaporated in nitrogen flow and the residue was dried and weighed to determine the percentage of soluble polymer and then, by difference the xylene insoluble fraction (%).

## **EXAMPLES**

### **Propylene polymerization: general procedure**

In a 4 liter autoclave, purged with nitrogen flow at 70 °C for one hour, 75 ml of anhydrous hexane containing 800mg of AlEt<sub>3</sub>, 79.8 mg of dicyclopentylmethoxysilane and 10 mg of



solid catalyst component were introduced in propylene flow at 30 °C. The autoclave was closed. 1.5 NI of hydrogen were added and then, under stirring, 1,2 Kg of liquid propylene were fed. The temperature was raised to 70°C in five minutes and the polymerization was carried out at this temperature for two hours. The non-reacted propylene was removed, the polymer was recovered and dried at 70 °C under vacuum for three hours and, then, weighed and fractionated with o-xylene to determine the amount of the xylene insoluble (X.I.) fraction at 25 °C.

#### **Ethylene polymerization: general procedure**

In a 4 liter autoclave, purged with nitrogen flow at 70 °C for one our, 1500 ml of anhydrous hexane containing 3 mMols of triethyl aluminium were introduced in nitrogen flow at 30 °C. Subsequently, a suspension of 20 mg of the solid catalyst component in 100 ml of hexane, containing 1.3 mMols of triethyl aluminium, were added at the same temperature. The autoclave was closed, 4 bar of hydrogen were added and the temperature was raised to 75°C in five minutes. Then, 7 bar of ethylene were added. The polymerization was carried out at this temperature for two hours. The non-reacted ethylene and the hexane were removed, the polymer was recovered and dried at 70 °C under vacuum for three hours and, then, weighed and analyzed.

#### **Preparation of $\text{MgCl}_2 \cdot (\text{EtOH})_m(\text{ROH})_n$ general procedure**

In a 2.5 L glass reactor equipped with thermometer, mechanical stirrer, reflux condenser, and purged with nitrogen, 250 mL of paraffin oil (OB55), a weighted amount of  $\text{MgCl}_2$  (see Table 1), ethyl alcohol (amount in Table 1) and, optionally, the additional alcohol (type and amount in Table 1) were introduced at room temperature under nitrogen flux. The stirring was started and the temperature raised until the solid phase disappeared. The temperature was kept constant for 2 hours under stirring. A second portion of the same paraffin oil (450 mL) maintained at the same temperature was then added to the  $\text{MgCl}_2$ /alcohol/paraffin mixture. The stirring was then raised to 1100 RPM to obtain an emulsion of the two phases. After 0.5 min of stirring, the emulsion was transferred under nitrogen flux to a second 5 L glass reactor containing 1500 mL hexane under stirring (350-400 RPM) at -15÷-20°C. The suspension was stirred 2 h at -10°C, then the temperature was raised to 0°C in 20 min, the stirring was continued 1 hour at this temperature. The temperature was raised to 10°C in 20 min and, after 1 h, it was raised again to 25°C. The stirring was continued for 2 hours at 25°C and then the mixture was allowed to settle and left to stay at 25°C overnight.

The solid  $\text{MgCl}_2\text{m}(\text{EtOH})_n(\text{ROH})$  spherical support was recovered by filtration, washed twice with 400 mL of hexane and once with 400 mL of pentane and finally dried under vacuum.

**Preparation of solid catalyst component: procedure A.**

Into a 500ml four-necked round flask, purged with nitrogen, 250 ml of  $\text{TiCl}_4$  were introduced at 0°C. Then, were added under stirring 10.0 g of the adduct prepared according to the general method described above and an amount of 2-isopropyl-2-isopentyl-1,3-dimethoxypropane as internal donor such as to give, with respect to Mg, a molar ratio of 6. The temperature was raised to 120 °C and maintained for 60 min. Then, the stirring was discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off.

250 ml of fresh  $\text{TiCl}_4$  were added. The mixture was reacted at 120°C for 30 min and, then, the supernatant liquid was siphoned off.

Again, 250 ml of fresh  $\text{TiCl}_4$  were added. The mixture was reacted at 120°C for 30 min and, then, the supernatant liquid was siphoned off. The solid was washed six times with anhydrous hexane (6 x 100 ml) at 60 °C. Finally, the solid was dried under vacuum and analyzed. The amount of diether (ID wt %) and the amount of Ti (wt %) contained in the solid catalyst component are reported in table 2.

**Preparation of solid catalyst component: procedure B.**

The same catalyst preparation procedure described in the procedure A has been followed, except that no internal donor has been used. The amount of Mg (wt%) and Ti (wt %) contained in the solid catalyst component are reported in table 2.

**Examples 1-12 and comparison examples 13-16**

The supports have been prepared according to the general procedure reported above. The specific conditions under which the supports have been prepared and the results of the analysis are shown in Table 1.

The catalyst components have been prepared according to the procedure A disclosed above and the characterization of the catalyst is shown in Table 2. The results obtained in the propylene polymerization carried out according to the general procedure reported above are summarized in Table 3.

**Examples 17 and 18**

The supports have been prepared according to the general procedure reported above. The

specific conditions under which the supports have been prepared and the results of the analysis are shown in Table 1.

The catalyst components have been prepared according to the procedure B disclosed above and the characterization of the catalyst is shown in Table 2. The results obtained in the ethylene polymerization carried out according to the general procedure reported above are summarized in Table 3.

**Example 19 and comparison example 20**

The supports prepared according to the procedure and conditions of example 3, and comparison example 14 respectively, have been used for preparing the catalyst components according to the procedure B. The characterization of the catalysts is shown in Table 2. The results obtained in the ethylene polymerization carried out according to the general procedure reported above are summarized in Table 3.

Table 1. Synthesis and characterization of MgCl<sub>2</sub> supports

Synthesis										Characterization							
Ex.	MgCl <sub>2</sub>		EtOH		ROH		T (°C)	Mg %wt	EtOH		ROH		m+n	n/(n+m)	H <sub>2</sub> O		
	g	g	g	g	R	g			%wt	m	%wt	n			%wt	%wt	p
1	38.9	56.0	Me	5.6	116	Me	5.6	10.7	46.1	2.27	4.3	0.30	2.58	0.12	0.50	0.06	
2	42.2	65.9	Me	5.0	115	Me	5.0	10.6	52.1	2.59	4.0	0.29	2.88	0.10	0.64	0.08	
3	37.7	52.3	Me	8.0		Me	8.0	10.3	47.2	2.42	7.0	0.52	2.93	0.18	0.64	0.08	
4	37.0	58.7	Me	10.2	107	Me	10.2	9.5	50.85	2.82	8.4	0.67	3.49	0.19			
5	38.0	57.3	Me	13.3	108	Me	13.3	9.6	47.85	2.63	12.2	0.96	3.59	0.27			
6	40.9	76.2	Me	3.7	114	Me	3.7	9.5	54.7	3.04	5.95	0.48	3.51	0.14	0.90	0.13	
7	40.6	71.0	Me	12.6	113	Me	12.6	8.8	53.3	3.20	9.9	0.85	4.05	0.21	0.50	0.08	
8	36.7	70.0	Me	7.0	106	Me	7.0	8.8	57.4	3.44	6.0	0.52	3.96	0.13	0.34	0.05	
9	41.6	65.4	n-Bu	10.5	115	n-Bu	10.5	10	50	2.64	10.4	0.34	2.98	0.11	0.5	0.07	
10	41.2	64.8	sec-Bu	10.4	114	sec-Bu	10.4	9.8	54.2	2.92	7	0.23	3.15	0.07	0.4	0.06	
11	42.2	66.4	i-Pr	8.7	118	i-Pr	8.7	10.6	48.4	2.41	5.85	0.18	2.59	0.07	0.6	0.08	
12	40.4	63.5	2-Me1-Pe	14.1	119	2-Me1-Pe	14.1	10	54	2.85	13.3	0.32	3.17	0.10	0.4	0.05	
13 comp	36.7	58.6	-	-	116	-	-	10.8	53.5	2.61	-	-	2.61	0.00	0.45	0.06	
14 comp	41.8	70.8	-	-	119	-	-	10.4	59.5	3.02	-	-	3.02	0.00	0.50	0.06	
15 comp	22.1	64.1	-	-	98	-	-	9.5	61.8	3.43	-	-	3.43	0.00	0.50	0.07	
16 comp	41.1	84.7	-	-	114	-	-	9.2	62.8	3.60	-	-	3.60	0.00	0.53	0.08	
17	25.3	42.2	Me	8.3	117	Me	8.3	10	47.95	2.53	9.3	0.71	3.24	0.22	0.65	0.09	
18	33.5	39.9	Me	11.1	115	Me	11.1	8.8	42.2	2.53	11.1	0.96	3.49	0.27	0.76	0.12	

Table 2. Composition of solid catalyst

Example	ROH	Procedure	Ti %	Mg %	ID %
1	MeOH	A	3.8	16.7	14.6
2	MeOH	A	4.2	17.3	14.0
3	MeOH	A	3.9	16.7	18.6
4	MeOH	A	4.8	21.6	15.1
5	MeOH	A	4.2	16.2	13.6
6	MeOH	A	3.9	16.8	13.9
7	MeOH	A	3.9	15.7	12.7
8	MeOH	A	4.4	16.8	13.9
9	n-BuOH	A	3.8	15.6	11.6
10	i-PrOH	A	3.4	14.1	12.1
11	sec-BuOH	A	3.7	15.4	11.6
12	2-Me-1-Pentanol	A	3.9	17.1	8.7
13 comp	no	A	3.7	17.1	15.3
14 comp	no	A	4.0	17.2	13.2
15 comp	no	A	3.4	16.6	17.6
16 comp	no	A	3.8	15.7	12.2
17	MeOH	B	7.5	14.0	----
18	MeOH	B	8.7	15.5	----
19	MeOH	B	9.4	15.3	----
20 comp	no	B	8.9	14.5	----

Table 3. Polymerization tests

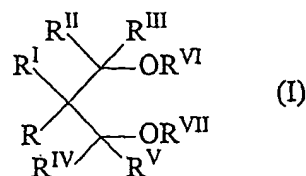
Example	Monomer	Yield Kg/g	XI %	MIL g/10'	MIE g/10'	F/E
1	Propylene	75	96.6	1.4	---	---
2	Propylene	94	96.8	5.5	---	---
3	Propylene	88	97	1.6	---	---
4	Propylene	93	97.8	5.7	---	---
5	Propylene	86	96.6	6.8	---	---
6	Propylene	72	97.1	1.9	---	---
7	Propylene	101	96.3	6.1	---	---
8	Propylene	93	96.6	5.6	---	---
9	Propylene	80	96.8	5.7	---	---
10	Propylene	76	96.7	5.7	---	---
11	Propylene	77	97.1	6.4	---	---
12	Propylene	93	96.2	5.4	---	---
13 comp	Propylene	67	97	2.1	---	---
14 comp	Propylene	75	97.1	8.9	---	---
15 comp	Propylene	64	96.8	2.7	---	---
16 comp	Propylene	79	96.3	3.3	---	---
17	Ethylene	16	-	-	0.63	50.8
18	Ethylene	13	-	-	0.35	50.3
19	Ethylene	17	-	-	1.3	40
20 comp	Ethylene	9	-	-	0.5	45

## CLAIMS

1. A  $\text{MgCl}_2 \cdot (\text{EtOH})_m (\text{ROH})_n (\text{H}_2\text{O})_p$  adduct in which R is a C1-C15 hydrocarbon group different from ethyl, optionally substituted with heteroatoms containing groups, n and m are indexes, higher than 0, satisfying the equations  $(n+m) \geq 0.7$  and  $0.05 \leq n/(n+m) \leq 0.95$  and p is a number ranging from 0 to 0.7 with the proviso that when R is methyl and  $(n+m)$  is in the range of 0.7 to 1, the value of  $n/(n+m)$  ranges from 0.05 to 0.45.
2. The adduct according to claim 1 characterized by the fact that  $(n+m)$  is higher than 1.
3. The adduct according to claim 2 characterized by the fact that  $(n+m)$  ranges from 2 to 5.
4. The adduct according to claim 1 characterized by the fact that the value  $n/(n+m)$  ranges from 0.1 to 0.4
5. The adduct according to claim 4 characterized by the fact that the value  $n/(n+m)$  ranges from 0.15 to 0.35.
6. The adduct according to claim 1 characterized by the fact that the index p ranges from 0.01 to 0.6.
7. The adduct according to claim 6 characterized by the fact that the index p ranges from 0.01 to 0.4.
8. The adduct according to claim 1 characterized by the fact that R groups are methyl or C3-C10 saturated hydrocarbon groups.
9. The adduct according to claim 1 characterized by the fact that the ROH alcohols are selected from the group consisting of methanol, propanol, isopropanol, butanol, sec-butanol, tert-butanol, pentanol, 2-methyl-1-pentanol 2-ethyl-1-hexanol phenol, 4-methyl-1-phenol, 2,6-dimethyl-1-phenol, cyclohexanol, cyclopentanol.
10. The adduct according to claim 9 characterized by the fact that the ROH alcohol is methanol.
11. A catalyst component for the polymerization of olefins comprising the product obtained by contacting a transition metal compound of groups 4 to 6 of the Periodic Table of Elements (new notation) with an adduct according to anyone of the preceding claims.
12. The catalyst component according to claim 11 in which the transition metal is selected from titanium compounds of formula  $\text{Ti}(\text{OR})_n \text{X}_{y-n}$  in which n is comprised between 0 and y; y is the valence of titanium; X is halogen and R is an alkyl radical having 1-8 carbon atoms or a COR group.
13. The catalyst component according to claim 12 in which the titanium compound is

selected from  $\text{TiCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{Ti}(\text{OBu})_4$ ,  $\text{Ti}(\text{OBu})\text{Cl}_3$ ,  $\text{Ti}(\text{OBu})_2\text{Cl}_2$ ,  $\text{Ti}(\text{OBu})_3\text{Cl}$ .

14. The catalyst component according to claim 11 which further contains an electron donor compound.
15. The catalyst component according to claim 14 in which the electron donor is selected from the alkyl or aryl esters of mono or polycarboxylic acids.
16. The catalyst component according to claim 14 in which the electron donor is selected from 1,3 diethers of the formula:



wherein R,  $\text{R}^{\text{I}}$ ,  $\text{R}^{\text{II}}$ ,  $\text{R}^{\text{III}}$ ,  $\text{R}^{\text{IV}}$  and  $\text{R}^{\text{V}}$  equal or different to each other, are hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and  $\text{R}^{\text{VI}}$  and  $\text{R}^{\text{VII}}$ , equal or different from each other, have the same meaning of  $\text{R}-\text{R}^{\text{V}}$  except that they cannot be hydrogen; one or more of the  $\text{R}-\text{R}^{\text{VII}}$  groups can be linked to form a cycle.

17. The catalyst component for the polymerization of olefins according to claim 11 characterized by the fact that before being contacted with the transition metal compound, the adduct is subject to a dealcoholation treatment.
18. Catalyst for the polymerization of olefins comprising the product obtained by contacting a catalyst component according to one of the claims 11 to 17, and an aluminum alkyl compound.
19. The catalyst for the polymerization of olefins according to claim 18 in which the aluminum compound is an Al-trialkyl compound.
20. The catalyst for the polymerization of olefins according to claim 19 further comprising an external donor.
21. The catalyst for the polymerization of olefins according to claim 20 in which the external donor is selected from the silane compounds containing at least a Si-OR link, having the formula  $\text{R}_a^1\text{R}_b^2\text{Si}(\text{OR}^3)_c$ , where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4;  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$ , are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms.



22. Process for the polymerization of olefins of formula  $\text{CH}_2=\text{CHR}$ , in which R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms, carried out in the presence of a catalyst according to one of the claims 18-21.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP2004/002519

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 C08F4/02 C08F10/00 C08F10/06 C08F4/654		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 123 767 A (ENICHIMICA SECONDARIA) 7 November 1984 (1984-11-07) cited in the application page 4, line 20 - line 24 examples 1,4,11	1,2, 4-15, 17-19,22
X	EP 0 544 340 A (ENICHEM ELASTOMERS) 2 June 1993 (1993-06-02) page 2, line 43 - line 49 page 3, line 15 - line 17 claims; examples	1-15, 17-19,22
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the International filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the International filing date but later than the priority date claimed *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *Z* document member of the same patent family		
Date of the actual completion of the International search 27 May 2004		Date of mailing of the International search report 23/06/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Thomas, D

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A	<p>DATABASE WPI Section Ch, Week 199130 Derwent Publications Ltd., London, GB; Class A17, AN 1991-218933 XP002282469 MIYA SHINYA; ONO KATSUHIKO: "Catalyst prepn. for olefin polymerisation - involves heat-stirring magnesium complex cpd. in presence of nonionic surfactant, cooling and treating with titanium halide, etc." &amp; JP 03 140308 A (CHISSO CORP) 14 June 1991 (1991-06-14) abstract</p> <p>-----</p>	1-22

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